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1 July - 30 September 1965

ELECTROCHEMICAL STUDIES IN THE SYNTHESIS  
OF N-F COMPOUNDS

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TRACOR, INC. 4525 ED BLUESTEIN BLVD., AUSTIN, TEXAS 78721

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Abstract

The electrolysis of  $\text{NH}_4\text{F}$  in anhydrous HF at various concentrations and anode potentials was studied during the past quarter.

If water is present in the electrolyte, the proportion of  $\text{N}_2\text{F}_2$  is decreased and  $\text{OF}_2$  and  $\text{NF}_3$  are increased. It is apparent that water has a large effect on the electrode reactions and thus cannot be used as a passivator to decrease attack of the anode during electrochemical fluorinations.

Additional studies were made to determine the conditions required for passivation of electrodes in liquid HF electrolytes.

## ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

## I. INTRODUCTION

Past work on this project has shown that the fluorination of  $\text{NH}_4^+$  in AHF does not occur by a potential-dependent stepwise reaction. In anhydrous HF electrolytes, corrosion of the anode material, nickel and Monel, occurs to the extent of about 10% of the current passed. The corrosion products accumulate on the electrode surface and strongly absorb quantities of fluorine evolved by the anode. Thus, the fluorination of species in the electrolyte probably occurs by chemical fluorination by fluorine trapped in the anode film. The increase in diffusion control through the anode film, the occurrence of both chemical and electrochemical oxidations, and changes in electrode character make the electrode kinetics exceedingly complicated.

Recent work has shown that nickel anodes can be passivated by the presence of as little as 0.01%  $\text{H}_2\text{O}$  in the electrolyte. Moreover, the passivity persists after passage of sufficient current to decompose all the water. Current work given in this report shows that the presence of water has a large effect on the relative proportion of various species in the volatile products formed by electrochemical fluorination of  $\text{NH}_4^+$ ; however, the persistence of passivity after decomposition of the water present makes it possible to use prepassivated electrodes for electrochemical fluorinations thereby decreasing the amount of current contributing to anode corrosion. It is also expected that the use of passive electrodes, which do not form bulky fluorine-saturated coatings, will allow observations of the true electrode behavior of anodic oxidation reactions in HF solutions.

Current work is devoted to obtaining quantitative analyses of the volatile and soluble products of electrochemical fluorinations

of  $\text{NH}_4^+$  in HF. Volatile product analyses are obtained by gas chromatography complemented by IR and mass spectra verifications of the species observed. Solution analyses are obtained by IR spectroscopy utilizing cells developed for this project. Additional work on electrode passivity is being performed to obtain the mode of electrical conduction through the fluoride film and to identify the species responsible for passivation of the electrode.

TABLE I

RELATIVE AMOUNTS OF VOLATILE PRODUCTS FORMED FROM THE ELECTROLYSIS OF  $\text{NH}_4\text{F}$  IN  $\text{NH}_4\text{F}$ 

$\text{NH}_4\text{F}$ CONCENTRATION	APPLIED CONSTANT POTENTIAL	% <sup>a</sup> $\text{F}_2$	% $\text{OF}_2$	% $\text{NF}_3$	% <u>trans</u> - $\text{N}_2\text{F}_2$	% $\text{x}$ <sup>b</sup>
0.04M	8.0 v	96.1%	~ 1.8%	1.1%	1.0%	-----
0.05M	10.0 v	95.0%	~ 0.1%	0.3%	4.6%	-----
0.10M	6.0 v	99.6%	-----	-----	0.4%	-----
0.10M	8.0 v	91.1%	~ 0.12%	0.1%	8.66%	~ 0.12%
0.10M	10.0 v	91.5%	~ 0.01%	~0.03%	8.46%	-----
0.87M	7.7 v	66.2%	~ 0.1%	0.14%	33.5%	~ 0.06%
1.0M	8.0 v	77.2%	~ 2.4%	2.1%	18.3%	~ 0.2%
2.0M	10.0 v	63.0%	~18.0%	12.8%	4.2%	-----

<sup>a</sup>% = percentage of product as found in the gas sample analyzed.<sup>b</sup> $\alpha$  = unidentified product.

## II. ANALYSIS OF ELECTROLYSIS PRODUCTS

A major portion of the work this past quarter has been devoted to the analysis of the volatile products formed from the electrolysis of  $\text{NH}_4\text{F}$  in HF. The products obtained were identified by gas chromatography and infrared and mass spectroscopy. The yields of the various products were studied as a function of both the applied potential and  $\text{NH}_4\text{F}$  concentration.

The procedure used for the GC work is described in Quarterly Reports 9 and 10 (1,2). The samples used for the IR and mass spectra were trapped from the GC exit line in 3 and 5 cc bombs immersed in liquid nitrogen. The IR spectrophotometer used is a Beckman IR 5-A, and the mass spectrograph used is a modified Electrodynamics Model 21-620 (m/e range of 2 to 150).

Table I shows the concentrations of the various species present in the volatile cell products as a function of applied potential and  $\text{NH}_4\text{F}$  concentration. The relative proportion of trans- $\text{N}_2\text{F}_2$  is affected by at least three factors:

1. The  $\text{NH}_4\text{F}$  concentration
2. The anode potential
3. The presence of  $\text{H}_2\text{O}$  in the electrolyte as indicated by the amount of  $\text{OF}_2$  formed (3).

An IR spectrum of a liquid electrolyte sample taken during an electrolysis of 5M  $\text{NH}_4\text{F}$  in AHF at 8.0 volts is shown in Figure 1. The spectrum has no absorption bands between 9.5 and 11.8 microns which can be attributed to  $\text{N}_x\text{F}_y^{n+}$ . The broad, strong  $\text{NH}_4^+$  bands are easily seen at 3.2, 6.0, and 7.15 microns. The weak  $\text{HF}_2^-$  band is seen at 6.5 microns and the broad, weak  $\text{H}_2\text{F}_3^-$  band between 8.6 and 9.2 microns. The portion of the spectrum between 10.8 and 11.9 microns is part of the background spectrum due to Irtran-2.

The presence of the various species in the volatile cell products was confirmed by IR and mass spectra. A portion of each sample trapped was used to obtain an IR spectrum which corresponded to the mass spectra identification. It should be noted that both the IR and MS (4) distinguish between cis- and trans-N<sub>2</sub>F<sub>2</sub>. Two strong absorption bands are obtained for cis-N<sub>2</sub>F<sub>2</sub> between 6.15 and 6.3 microns, while trans-N<sub>2</sub>F<sub>2</sub> has two strong bands at 10.1 and 10.3 microns. In the mass spectra, the strongest peak for cis-N<sub>2</sub>F<sub>2</sub> is mass 47 and the strongest peak for trans-N<sub>2</sub>F<sub>2</sub> is mass 28.

The product previously identified as cis-N<sub>2</sub>F<sub>2</sub> has been identified by its IR and mass spectra to be SiF<sub>4</sub>.

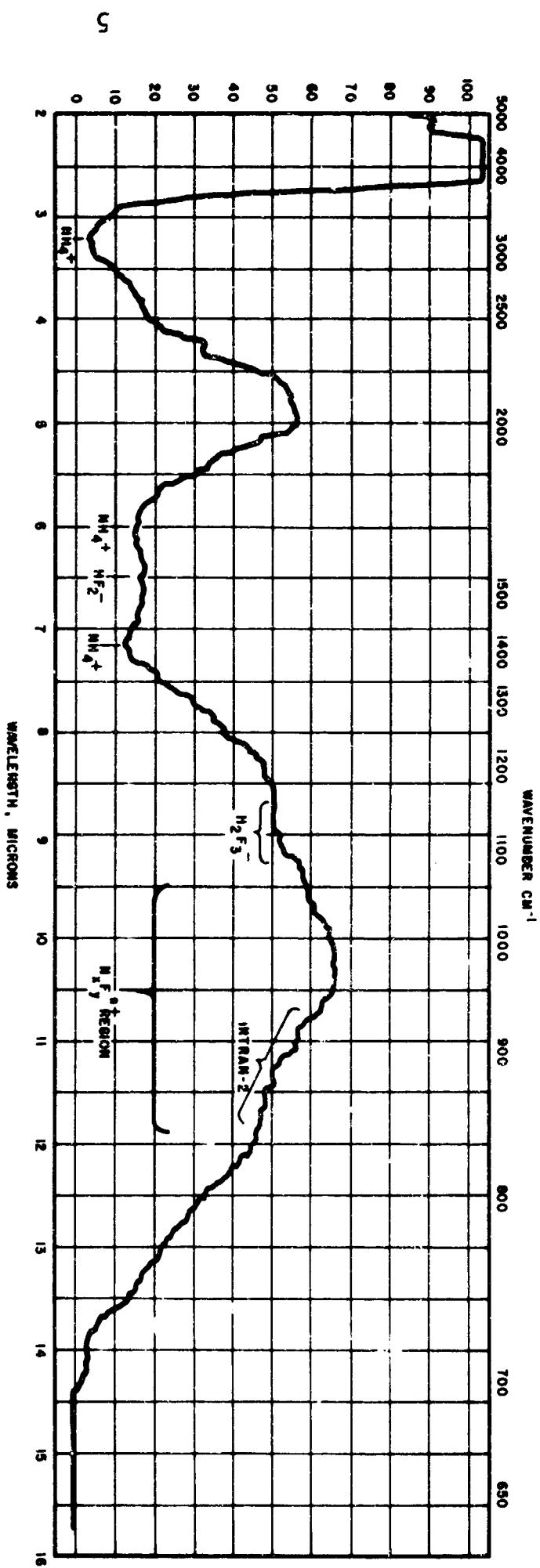


FIG. 1 - IR LIQUID SPECTRUM OF PRODUCTS OBTAINED FROM THE ELECTROLYSIS OF 5M  $\text{NH}_4\text{F}$  IN AHF AT +8.0 V.

SPECTRUM # 10-15-6581  
 DATE - OCT. 15, 1968  
 SAMPLE - +8.0 V ELECTROLYSIS SAMPLE FROM 5M  $\text{NH}_4\text{F}$  IN AHF SOLUTION  
 SOURCE -  
 STRUCTURE -  
 PATH - 0.05 mm  
 SOLVENT - HF  
 CONCENTRATION -  
 PHASE - LIQUID  
 COMMENTS - SLOW SCAN, TEMPERATURE = - 65°C  
 ANALYST - *George*

## III. ELECTROCHEMICAL STUDIES ON NICKEL

Differential capacity measurements were made on nickel electrodes in AHF and in HF plus 0.01% and 0.10%  $H_2O$ . The method of charging curves based on the application of a square-wave signal was used for making the measurements (5). This method is suitable for solid metal electrodes having geometrical areas as large as 2 to 3  $cm^2$ . All data reported here were taken on nickel electrodes with an area of 1  $cm^2$ . With this small electrode size and the circuit parameters listed below, differential capacities up to 10  $\mu F/cm^2$  are readily obtained with good accuracy. A block diagram of the electronic setup is shown in Figure 2. The pulse generator delivers a push-button triggered 10 mA, 15  $\mu sec$  pulse with a rise time of < 1  $\mu sec$ . The potential-time trace displayed on the oscilloscope (Tektronix 535A with a Type H preamp) was recorded with a Polaroid camera. The differential capacity is then calculated from the equation

$$c = I / \left( \frac{dE}{dt} \right)_{t=0}$$

where

$\frac{dE}{dt}$  = the slope of the potential-time trace.

Capacity data were taken during galvanostatic polarization runs. The polarization curves and differential capacity measurements are shown in Figures 3 and 4.

The current density during anodic polarization of nickel in AHF using a constant current source is somewhat higher than when using a constant potential source (1), but the general shape of the curves are the same. However, upon the addition of  $H_2O$ , the galvanostatic curves exhibit a behavior typical of a passivating electrode (i.e., a large increase in potential at a fixed current density until electrolyte decomposition occurs) (5). The current

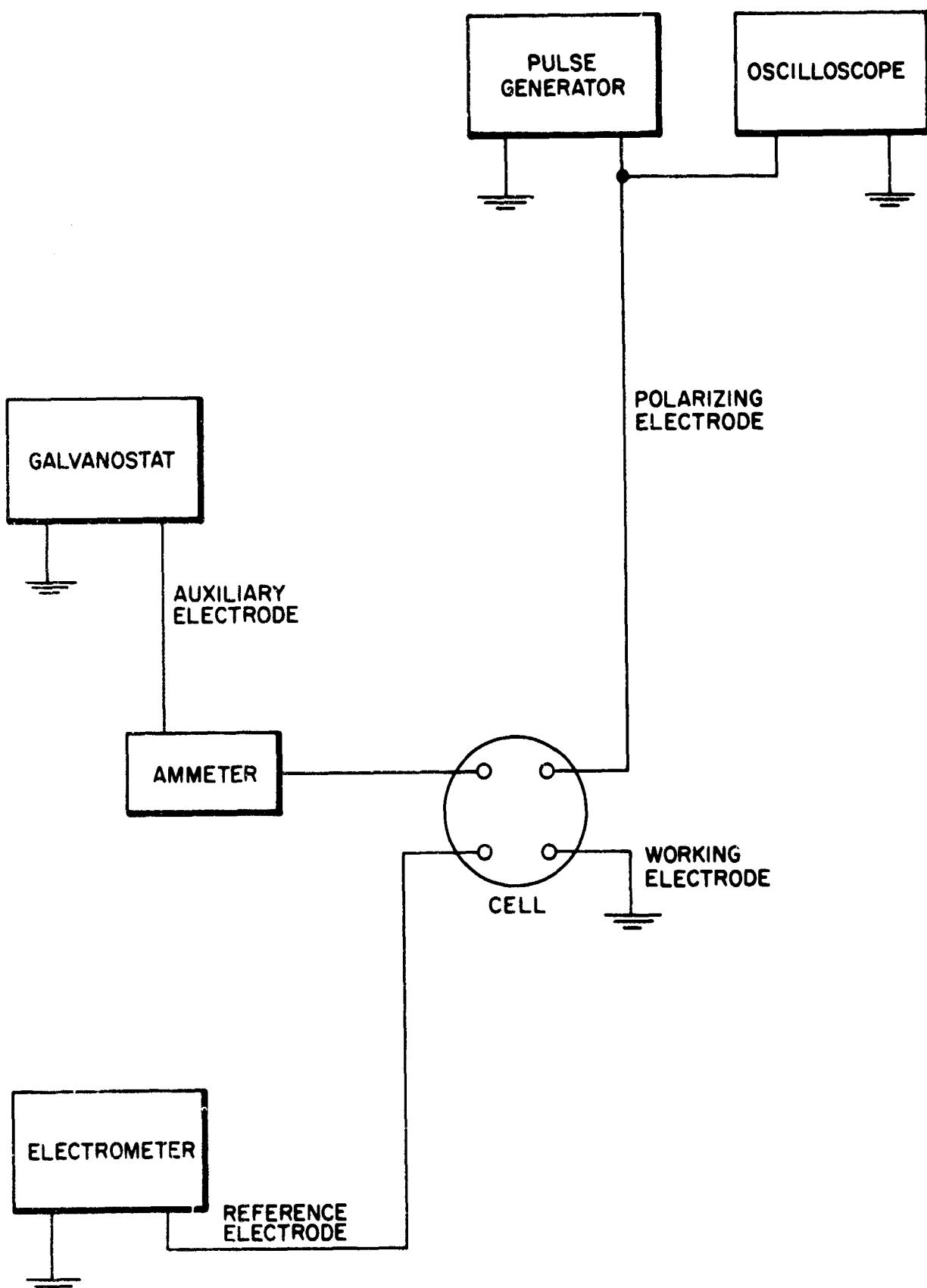


FIG. 2 - BLOCK DIAGRAM OF PULSING CIRCUIT

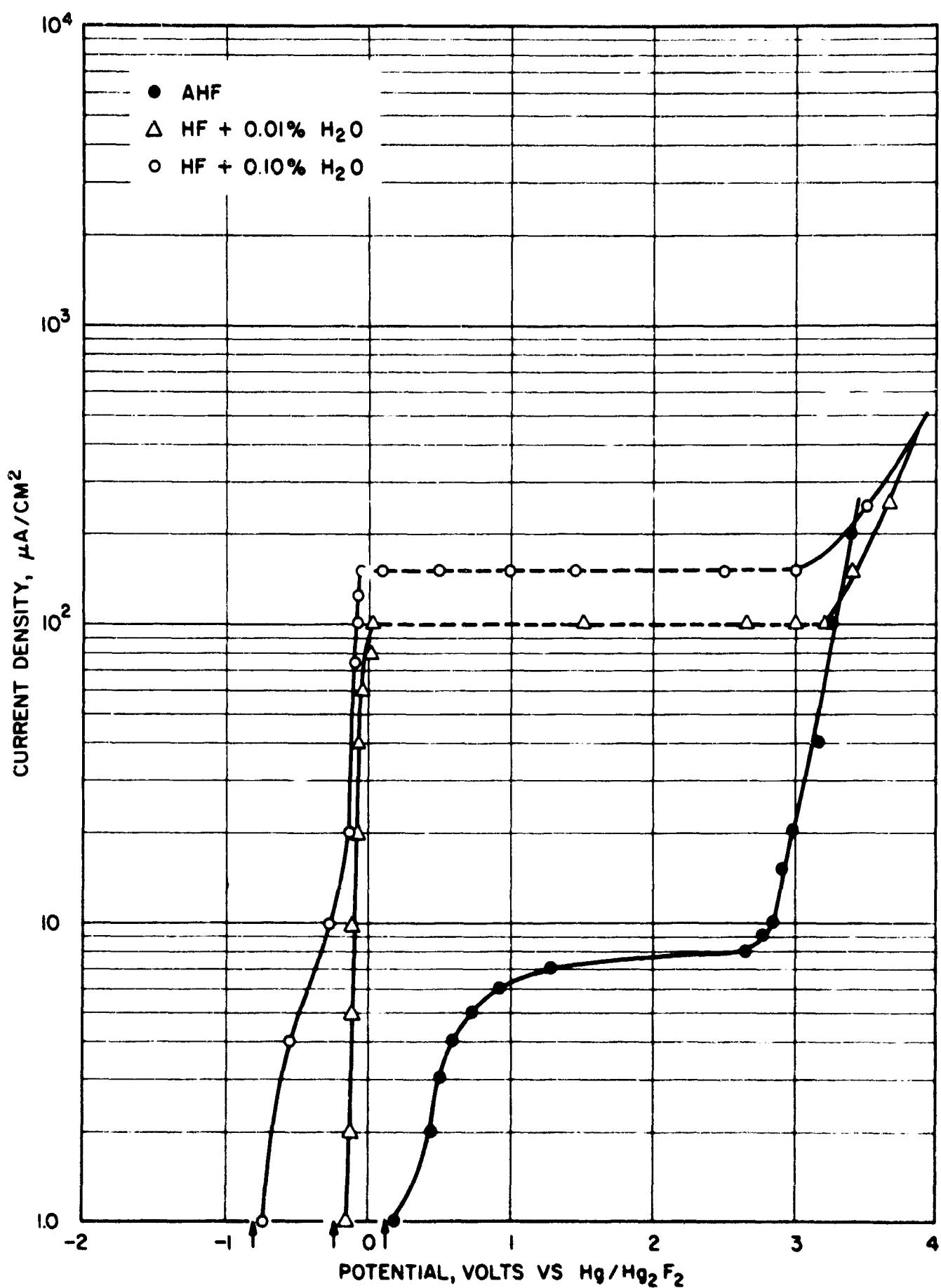


FIG. 3 - GALVANOSTATIC POLARIZATION CURVES OF NICKEL  
IN HF + 0.01M NaF

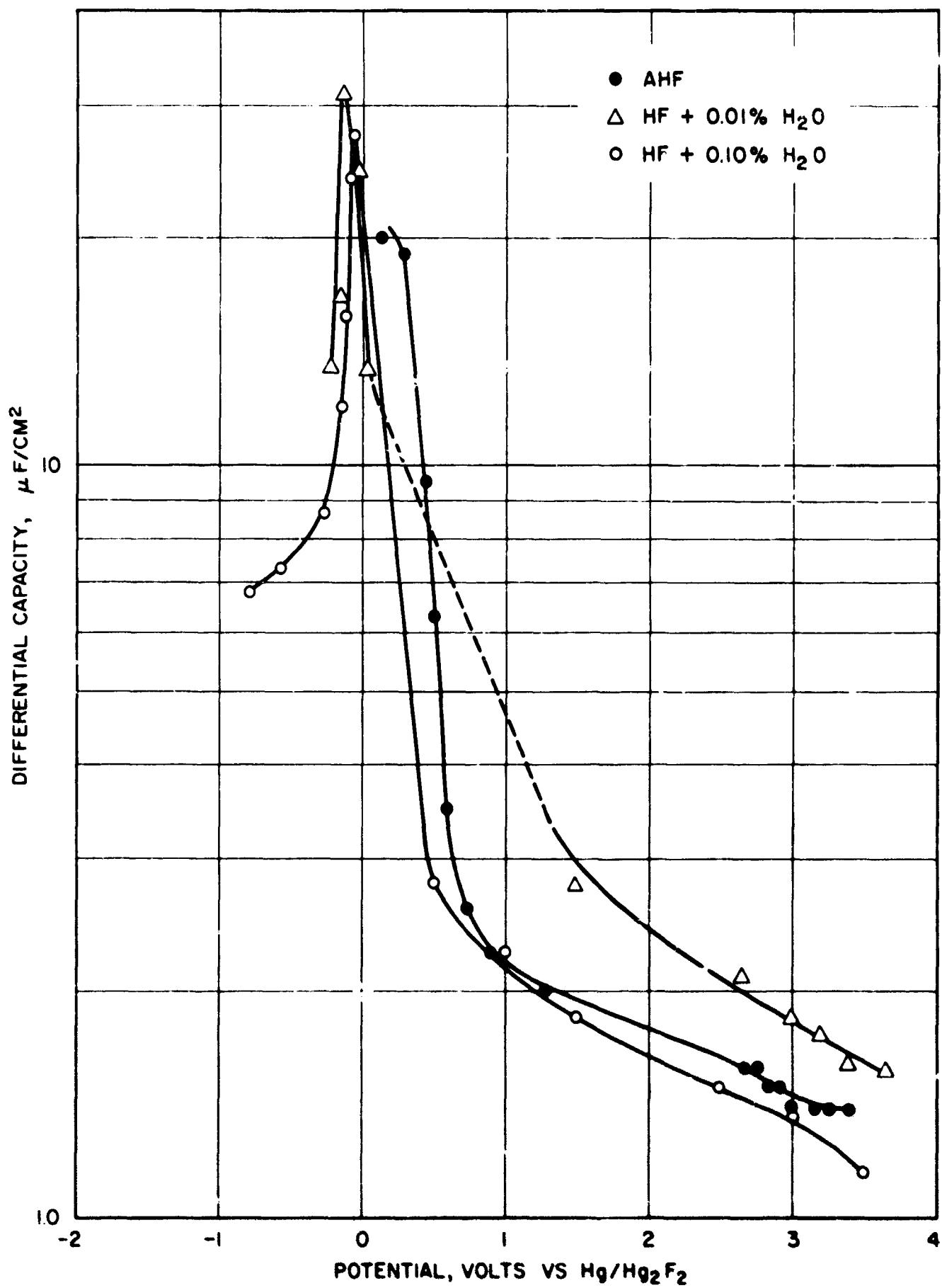


FIG. 4 - DIFFERENTIAL CAPACITY OF NICKEL  
 IN HF + 0.01M NaF

density increases with increasing water concentration as it did in the potentiostatic runs.

The differential capacity of the nickel electrode in AHF is about  $20 \mu\text{F}/\text{cm}^2$  at open circuit (Figure 4). This value is typical of those found on many metals in aqueous systems (6). Upon anodic bias, the differential capacity decreases rapidly to a value of about  $1.5 \mu\text{F}/\text{cm}^2$ . The addition of water causes the open circuit potential to shift cathodic and the differential capacity is lower at open circuit. Also a peak in the capacity curve is noted at about 0 volts vs  $\text{Hg}/\text{Hg}_2\text{F}_2$ . The initial low capacities may be due to adsorption of a cation (e.g.,  $\text{H}_3\text{O}^+$ ) which is reduced upon anodic bias causing the capacity to increase until initiation of the film formation. The differential capacity curves from 0 volts to the fluorine evolution potential show no consistent significant changes with water concentration.

The low capacities are attributed to the formation of a stable film on the electrode. The stability of the film is evidenced by the length of time required for the differential capacity to reattain its initial value. Figure 5 shows the change in capacity with time at open circuit. After 20 hours the capacities of the electrodes were still below their original values, and in the solution containing 0.10% water, even after several days, the capacity was below its original value.

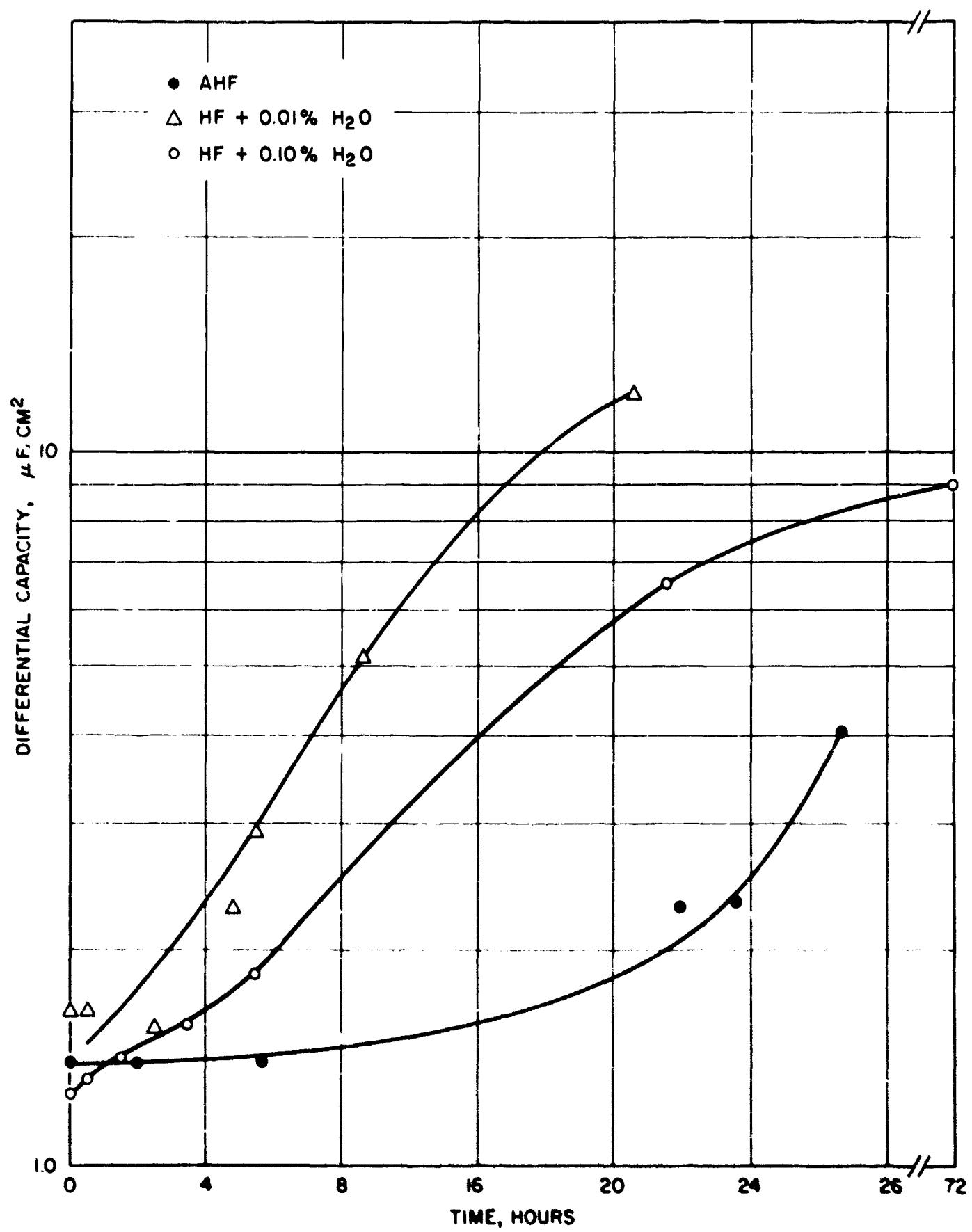


FIG.5 - CHANGE OF CAPACITY WITH TIME

## IV. DISCUSSION

Analysis of the electrolysis products formed in both vapor and liquid phases will be continued to obtain balances between current passed and the amount of products formed. The data obtained for the vapor phase are reproducible and accurate. Analyses of volatile cell products showing large proportions of  $N_2F_2$  under same conditions imply a strong possibility that intermediate ionic species exist during the electrochemical fluorination of  $NH_4^+$ . Confirmation of the existence of the intermediates may be accomplished by optimizing the yield of fluorinated nitrogen products (possibly by using passive electrodes) and by operating the cell at lower temperatures to prolong the life of the intermediates.

Differential capacity measurements on nickel electrodes in AHF plus 0.01M NaF show a value of about  $20 \mu F/cm^2$  at the open circuit. The capacity decreases rapidly upon anodic polarization to a steady reading of about  $1.5 \mu F/cm^2$ , indicating the formation of a film on the electrode. Addition of water lowers the differential capacity at open circuit, but the same behavior is observed upon anodic polarization. Galvanostatic polarization curves are typical of a passivating electrode when  $H_2O$  is present. However, the low capacity film is present in AHF as well as when water is present, indicating that the passivating film (formed with  $H_2O$  plus HF) and the film formed in AHF are at least similar in some respects.

V. FUTURE WORK

Electrochemical fluorinations of  $\text{NH}_4^+$  in anhydrous HF will be continued. Particular emphasis will be placed on the detection of soluble intermediate ionic species through the use of lower cell temperatures and optimum cell conditions. It is anticipated that the use of passive electrodes will result in a greater selectivity of product formation by control of the anode potential. The analytical methods and electrochemical techniques developed thus far will be applicable to investigations of the electrochemical fluorination of  $\text{N}_2\text{H}_5^+$  in anhydrous HF.

Investigations of passive electrodes will be limited to attempts to identify the extremely thin films formed during anodic polarization. These experiments will utilize X-ray and/or electron diffraction patterns obtained from nickel electrodes after anodic polarization in HF containing trace amounts of water.

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